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COMPLETE SPECIFICATION.

Treatment of Aluminum Oxide Coatings.

We, CHARLES CALVIN COHN and SAMUEL
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States of America, trading in co-partner-
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5 Ridge Avenue and Crawford Street, City of
Philadelphia, Commonwealth of Pennsylv-
ania, United States of America, do hereby
declare the invention, for which we pray
that a patent may be granted to us, and the
10 method by which it is to be performed, to
be particularly described in and by the
following statement:—

This invention relates to the treatment of
aluminum oxide coatings of porous type
15 artificially formed on aluminum or alumi-
num-base alloys to produce increased resis-
tance to corrosion, the treatment involving
specifically the use of alkali metal silicates.
Hereafter, for convenience, aluminum and
20 aluminum-base alloys will be collectively
designated as aluminum.

Porous coatings to which the treatment
described herein applies are such as are pro-
duced on aluminum by anodizing or by
25 chemical treatment in particular ways. The
coatings, as produced by anodizing, involve
anodizing in such electrolytes as are typified
by sulfuric acid (or equivalent bisulfate),
phosphoric acid, chromic acid, sulphamic
30 acid, oxalic acid, or other electrolytes pro-
ducing similar results. The oxide coatings
thus produced are porous, in contrast with
those produced by anodic treatment in boric
acid, ammonium bicarbonate, or similar
35 electrolytes which produce coatings of such
low porosity that the matters to be herein
described are inapplicable.

Other porous coatings to which the pre-
sent invention is applicable are producible
40 by chemical oxidation and are typified by
those produced by the use of alkali chromates
combined with sodium carbonate, or by the

use of baths containing fluorine ions and
chromic ions, in some cases with the addi-
tion of phosphoric ions, e.g., an aqueous acid
45 bath comprising chromic acid, sodium bi-
fluoride, sodium fluoborate and a sodium
phosphate.

The production of porous oxide coatings,
both electrolytically and by non-electrolytic
50 chemical action, is well-known, and it is un-
necessary to describe the details of the pro-
cesses used which are widely applied in this
art. The present invention is quite gener-
ally applicable to the porous coatings so
55 produced.

Alkali metal silicates have been used in
the treatment of porous aluminum oxide
coatings in attempts to protect such coatings
against corrosion. However, the corrosion
60 resistance developed by known methods has
not been satisfactory because they merely
deposit loose, sparingly absorbable protec-
tive films most of which may be easily wiped
from the coatings. A coating protected by
65 such a film may, directly after forma-
tion, stand up under the usual corrosion
resistance tests. But when the coating is
first wiped and then tested, the coating from
which the film is more or less removed will
70 not stand up satisfactorily. Further, in the use
of known methods of using silicates the
relatively loose protective film becomes
chalky when exposed to air, and the surface
readily becomes streaked.
75

The general object of the present inven-
tion may be briefly stated as that of pro-
ducing greatly improved corrosion resistance
through the use of alkali metal silicates but
with the silicates involved in a fashion which
80 is, apparently, one not involving a mere
coating of the aluminum oxide coating. This
is indicated by the fact that even when
thoroughly wiped down the coating not only

[Pr

has exceptional corrosion resistance but also retains its initial uniform appearance.

The invention is characterized by the use of successive steps. In the first step of the treatment here involved (which may be preceded by other steps not related directly to the invention) a preliminary treatment of the porous oxide coating is effected by the use of a silicate solution under conditions which fall short of producing sealing action. Either sodium or potassium silicate may be used, but since sodium silicate is considerably less costly it constitutes the commercial chemical and reference will be specifically made hereafter to the use of sodium silicate, with the understanding that equivalent quantities of potassium silicate may be used. Preferably the first treatment is carried out at a temperature less than 120° F., (if successive treatments are carried out in different silicate baths) and best results have been secured when the temperature used is around room temperature up to about 110° F. The time of this treatment should be relatively short: 1/2 minute to 5 minutes. For the first treatment the ratio of silica to alkali metal oxide should be at least 2:1. The concentration of the silicate may range from about 1 gram per liter to saturation, this range involving equivalent concentrations of silicate ranging from about 0.1% to 30%. The maximum concentrations used will depend upon the solubility of the particular silicates involved, high concentrations being undesirable when the viscosity of the silicate solution becomes unduly high causing it to adhere to the work being treated.

Times of treatment are not critical, but in this first step they should desirably be less than about five minutes, two minute treatment being generally sufficient, longer times of treatment being undesirable particularly when the silica to soda ratio is low, giving alkalinity conditions which may cause objectionable etching.

The action which occurs in this first step is open to conjecture, but it seems probable that aluminum silicate is formed producing a reduction of pore size. It is not desirable to carry out this step at temperatures above 120° F. (still referring to successive treatments in different silicate baths) because then there may be hydration impeding the desirable action of the first step. Whatever occurs in the first step should become complete or effective before any substantial degree of hydration may occur.

But alternative to what has just been described is a first treatment in the same silicate bath as that used in the second step and at an elevated temperature. In this case advantage is taken of the fact that sealing with silicate is a function of both temperature and time and sealing is prevented if, even though the coated aluminum articles

are immersed in a hot silicate solution, they are quickly removed therefrom and held in the air for a short time before being again immersed in the silicate solution for the final treatment. The explanation is probably that, because the articles cool off very rapidly upon removal from the bath, the same action takes place as occurs if the initial treatment took place at a considerably lower temperature. For example, considering a bath of sodium silicate having a ratio of silica to sodium oxide of 2:1, with a silicate concentration of 5 grams per litre, and maintained at 210° F., an immersion of the coated aluminum articles for 1 minute or less followed by removal into the air for 1/2 minute to 1 minute or more before a second immersion in the same bath, gives results substantially the same as those previously discussed. Apparently this is due to the fact that the first immersion effectively only wets the articles and the first step is primarily carried out after the removal at an average temperature so decreased that the sealing which is to be avoided does not occur.

In commercial practice the time of the first immersion usually has a lower limit of about 1/2 minute because the articles carried by racks must be handled by hoists, the most rapid operations of which in effecting dipping and removal take times of the order of 1/2 minute; in other words, while dipping for less time would theoretically suffice, it cannot practically be carried out substantially faster.

The advantage of using the same bath for both the first and second treatments is, obviously, economy and facilitation of operation. Preferably, to avoid substantial sealing in the first treatment the single bath in such case is operated at a temperature relatively low in the range for good results in the second treatment, e.g. as low as 150° F., thereby giving more leeway in the permissible time of immersion in the first treatment. For example, if the bath is at 150° F., the first immersion may take as long as about 5 minutes as compared with little more than 1 minute if the bath is at 210° F. As will more fully appear hereafter, the second treatment must be correspondingly prolonged if the bath temperature is thus maintained low.

It may seem, on casual consideration, that a double immersion in the same bath would only be equivalent to continuous immersion in the bath; but this is definitely not the case. Apparently whatever reaction occurs as a result of the first immersion takes some time (though short) and for proper results must be completed by withdrawal of the articles into the air, with resulting cooling, before they are subjected to substantial sealing action of the silicate. Attempts to secure

the desired results in a single immersion have been completely unsuccessful.

In an alternate first step of the treatment, hydration of the porous oxide is effected by a hot water treatment, which in its simplest form may involve the use of water alone. The action which occurs in this first step is open to conjecture but it seems probable that the significant effect is the reduction of the pore size by reason of swelling of the oxide. The sealing thus produced, however, is far from complete so that the coating remains essentially porous, although the porosity may be said to be substantially reduced. Generally speaking, however, it is desirable to use in this step not plain water but a solution which augments the effect of the water in one of several ways. Using some aqueous solutions under heated conditions, the water of the solution not only effects swelling and reduction of pore size, but the solute is of a type which is adsorbed by the coating to augment, by reason of the added adsorbed material, the reduction of the effective size of the pores. The aqueous solution in a second form may contain a material which, under the hot conditions of application, will precipitate within the pores, and thus augment the reduction of their size, by the plugging action of an insoluble material. Typical of this type of treatment is the use of readily hydrolyzable salts such as nickel or cobalt acetates. In a third type of aqueous solution thus used, there is (according to some theories) both reaction with the aluminum oxide coating or the base aluminum and adsorption, solutions of this type being typified by those of alkali dichromates.

In accordance with the present invention, the first treatment, carried out in one of the above fashions just indicated, is followed by a second treatment involving the use of an alkali metal silicate in hot aqueous solution. Either sodium or potassium silicate may be used, but from the practical standpoint sodium silicate is least expensive and is generally used. This second step of the treatment involves the subjection of the coating, following the application of the first step, to the action of a solution of alkali silicate which has a concentration of silicate in the range from one gram per litre to saturation, the latter depending upon the particular silicate which may be used. The concentration of silicate may range from about 0.1% to 30%. Generally speaking, the concentration of silicate in its solution is conveniently about ten grams per liter, though this concentration is far from critical. As to the silicates used, they may involve a ratio of silica to alkali metal oxide in the range of about 1:1 to about 4:1. The temperature of the treatment is desirably above 150° F. and may range up to the boiling point. Temperatures for this second step are preferably

in the range from 190° F. to the boiling point of the solution. The time of treatment of the articles may range from 5 to 30 minutes. If the silica to soda ratio is low, temperatures of treatment in the lower portion of the temperature range should be used to minimize etching action. More extended treatment than 30 minutes is harmless but also has very little useful effect. Practical considerations indicate that treatment ranging from five to twenty minutes is very satisfactory. While the last discussion is generally worded to cover procedures in which the first and second treatments are carried out in different baths, it will be understood from the earlier discussion that, in the case of baths of an alkali metal silicate solution, the bath for the second treatment may be that used in the first treatment, with the indicated precautions being taken to prevent substantial sealing in the first treatment and to effect completion thereof, while the second treatment is carried out to complete sealing.

In the case of the specific examples referred to below it may be assumed that the aluminum articles are anodically coated in a 15% (by weight) sulfuric acid solution in water with a current density of twelve amperes per square foot of alternating current for from 5 to 60 minutes at 75° F. in accordance with conventional practices. The articles are then washed with water and given treatments in accordance with the invention. While specific reference has been made to one anodizing procedure, this is merely for illustrative purposes and has no basic significance, any oxide-forming coating process being usable which provides a porous aluminum oxide film, as already described. The choice of one oxide coating procedure over another is generally dictated only by particular specific results desired such as the thickness or density of the coating.

Specific examples of procedures in accordance with the invention are the following:

EXAMPLE I.

Anodically porous-coated aluminum articles are immersed for 2 minutes in an aqueous solution at 120° F. containing 5 grams of sodium silicate per liter, the silica (SiO_2) to soda (Na_2O) ratio being 2:1. The articles are then sealed (no rinsing being necessary) by being immersed for 5 minutes in an aqueous solution at 200° F. containing 10 grams of sodium silicate per liter, the silica to soda ratio being 2:1.

EXAMPLE II.

Anodically porous-coated aluminum articles are immersed for 2 minutes in an aqueous solution at 120° F. containing 10

grams of sodium silicate per liter, the silica to soda ratio being 3.2:1. The articles are then sealed by being immersed for 5 minutes in an aqueous solution at 200° F. containing 10 grams of sodium silicate per liter, the silica to soda ratio being 3.2:1. For this sealing the ratio of silica to soda may be anywhere between 3.2:1 and 1:1 or more or less.

EXAMPLE III.

Anodically porous-coated aluminum articles are immersed for 5 minutes in an aqueous solution at room temperature containing 10 grams of sodium silicate per liter, the silica to soda ratio being 2:1. The articles are then sealed (no rinsing being necessary) by being immersed for 5 minutes in an aqueous solution at 190° F. containing 10 grams of sodium silicate per liter, the silica to soda ratio being 2:1.

The foregoing examples involve the use of separate baths for the initial and final treatments. Examples may now be given which involve successive immersions of the articles in the same bath.

EXAMPLE IV.

Anodically porous-coated aluminum articles are immersed for 1 minute in an aqueous solution at 210° F. containing 5 grams of sodium silicate per liter, the silica to soda ratio being 2:1. The articles are then removed and maintained in the air above the bath for 1 minute, after which they are again immersed in the same bath for 5 minutes.

EXAMPLE V.

The same procedure as in Example IV is carried out except that the times of the first immersion and the maintenance of the work in the air were reduced to the minimum practical commercial times of 1/2 minute, each. The results were identical with those of Example IV.

In a laboratory test the last procedure was carried out but with the time during which an article was held in the air between treatments reduced to 10 seconds. The results were still identical with those of Example IV.

The last two examples were carried out using aluminum articles containing porous coating produced, respectively, (1) by conventional treatment with an aqueous solution of 6 ounces per gallon of sodium carbonate and 2 ounces per gallon of sodium chromate, and (2) by conventional treatment with an aqueous solution containing, per liter, 3.7 grams of chromic acid (CrO_3), 0.75 grams of sodium bifluoride (NaHF_2), 0.7 grams of sodium fluoborate (NaBF_4) and 1.0 gram of trisodium phosphate for 5 minutes at 80° F. The results produced

were the same as in Example IV above.

A form of over-all treatment which has been found particularly satisfactory is that which involves in the first step the use of nickel acetate in aqueous solution. Such treatment not only gives excellent results when dyeing of the coat is not involved, but has especially advantageous applicability when dyeing is involved. The reason for this is that if a porous aluminum oxide coating is dyed in the usual fashion and is then treated with a silicate solution the dye is largely removed. However, if after dyeing the coating is subjected to the action of a hot nickel acetate solution, the subsequent treatment with the silicate solution does not remove the dye with the result that the advantageous results of the procedure in accordance with the invention may be secured in the case of dyed coatings.

EXAMPLE VI.

Anodically porous-coated aluminum articles are immersed in a 0.5% nickel acetate solution for about 5 minutes at a temperature of approximately 180° F. The articles are then washed with water and immersed in a sodium silicate solution having a concentration of ten grams per liter and a ratio of silica to soda of 2.4:1. The immersion is continued at a temperature of 190° F. for approximately 5 minutes. Finally, the articles are washed in water and dried. The result is a clear, smutless oxide coating which provides resistance to corrosion against both salt spray and alkali.

Remark may be here made concerning the absence of smut on the oxide coating. The use of nickel acetate frequently produces smut to a marked degree, but this, in accordance with this invention is effectively removed by the silicate treatment in all variants thereof producing acceptable corrosion resistance.

Wide variations may be made in the details of the foregoing treatment. The nickel acetate may be replaced by generally equivalent quantities of other hydrolyzable nickel salts or hydrolyzable salts of cobalt, for example. A considerable pH range of 4.5 to 7.5 of the nickel acetate or equivalent hydrolyzable salt may be used. The concentrations of the hydrolyzable salts are not critical, and may range from around 0.1% to saturation. The treatment may be carried out for a period ranging from around two to twenty minutes, and the temperature may range upwardly from around 120° F. to boiling, though a temperature of at least 150° F. is most desirable.

The range of composition and of temperatures and times of application of the sodium silicate solution may be as already described, the temperatures of the silicate solution being from room temperature up to boiling,

and the time of treatment ranging upwardly from 1/2 minute.

The step of washing between the first and second treatment of the coating may here be explained from its general standpoint. Where the material in solution in the first treatment may react with the silicate, a quite thorough rinsing is desirable since excess first solution (such as nickel acetate) would react with the silicate to produce not only possibly irregular results in the work but also deterioration of the silicate solution by precipitation of a nickel silicate therein. On the other hand, there are conditions in which it is immaterial whether the material from the first step of the treatment is possibly carried into the silicate solution, as where the first sealing is by water alone, or where the first treatment involves the use of a silicate solution which does not differ too markedly in composition from that used in the final treatment. The washing step, therefore, has its utility essentially in preventing undesired reaction, or contamination of the silicate solution.

EXAMPLE VII.

Anodically porous-coated aluminum articles are immersed for 1 minute in a 5% aqueous solution of sodium dichromate at 70° F. After a water rinse, the articles are sealed by being immersed for 5 to 10 minutes in a solution at 200° F. containing 10 grams per liter of sodium silicate, the silica to soda ratio being 2:1.

Variants of the last example may involve immersion in an aqueous sodium dichromate solution having a concentration of 0.1% to saturation for periods of 1 to 25 minutes and at temperatures ranging from 70° F. to boiling. The final sealing may be accomplished in sodium or potassium silicate solutions under any of the varied conditions heretofore discussed.

The sodium dichromate of this example may be replaced by another alkali dichromate, alkali chromates or chromic acid.

EXAMPLE VIII.

Example VII in all of its variations mentioned may be carried out by substituting sodium molybdate for the sodium dichromate. The concentration of the molybdate may range from 0.5% to saturation, a 1% concentration being highly satisfactory.

EXAMPLE IX.

Anodically porous-coated aluminum articles are immersed for 2 minutes in an aqueous solution at 150° F. containing 10 grams of disodium phosphate per liter. After a water rinse, the articles are sealed by being immersed for 5 minutes in an aqueous solution at 200° F. containing 10 grams per liter

of sodium silicate, the silica to soda ratio being 2:1.

Here, also, variations may be made as indicated in Example VII.

EXAMPLE X.

The procedure of Example IX may be carried out by substituting for the disodium phosphate solution a 1 gram per liter aqueous solution of tannic acid, at a preferred temperature of 120° F.

EXAMPLE XI.

The procedure of Example IX may be carried out by substituting for the disodium phosphate solution a 1 gram per liter aqueous solution of potassium permanganate. A temperature of 190° F. and an immersion time of 5 minutes are desirable.

It should be noted that plain hot water may be used for the initial treatment, desirably at or near boiling but for best results, the water temperature should be at least 150° F.

The sealed oxide coating produced in accordance with the foregoing examples will stand up for at least sixteen hours when subjected to a salt-spray test carried out with an aqueous solution containing 5% sodium chloride and one gram per gallon of cupric chloride, adjusted to a pH of 3.2 which acetic acid, the solution being maintained at a temperature of 120° F. Furthermore, sealed oxide coatings so produced will stand up for from eight to ten minutes when immersed in an aqueous solution containing 3% caustic soda and applied at 80° F. Such tests respectively indicate high resistance to salt spray corrosion and also to alkali corrosion.

With respect to the matter of both salt-spray and alkali-corrosion resistance, it may be noted that there has arisen a considerable demand in certain industries for such combined resistance. In the automobile industry, for example, washing compounds for cleaning cars are sometimes very high in alkalinity, in consequence of which they have a tendency to corrode anodized aluminum parts. In the architectural field, the corrosive actions of cement and mortars are often highly alkaline in nature, tending to corrode anodized aluminum.

As already indicated, a sodium silicate solution may be used for the initial treatment which is identical, as to concentration and silica to soda ratio, with the sodium silicate of the second sealing treatment, whether the same bath is used or different baths maintained at different temperatures. When sodium silicate is used for both the initial treatment and the second sealing treatment and the solution of the latter treatment is more highly concentrated than that of the initial treatment, a water rinse may be used between the first and sealing treatments.

Further, if the sodium silicates of the two treatments do not have the same silica to soda ratio, a water rinse may be used between the first and sealing treatments. This rinsing merely prevents change of composition of the second bath by carry-over from the first.

WHAT WE CLAIM IS:—

1. The method of treating aluminum having a porous oxide coating thereon which comprises first applying to the surface thereof an aqueous bath under time and temperature conditions to effect only partial sealing of the pores of the oxide coating, and then applying to the surface thereof an aqueous solution of an alkali silicate at a temperature in excess of about 150° F. for a period ranging from about 5 minutes to 30 minutes to complete sealing thereof.

2. The method according to Claim 1 in which said first bath is a hot aqueous solution of an alkali silicate.

3. The method according to Claim 2 in which said conditions of said first bath are such that the resulting reaction is completed while the pores are only partially sealed before the second treatment.

4. The method according to Claims 2 or 3 wherein after the first step of applying a hot aqueous solution of an alkali silicate, the thus treated aluminum is exposed to the cooling effect of air to complete the resulting reaction before the second treatment.

5. The method according to any of the preceding claims wherein said successive applications of aqueous solution are made with the same aqueous solution of alkali silicate.

6. The method according to Claim 5 in which said first application of an aqueous solution of alkali silicate occurs at a tem-

perature not in excess of about 120° F. for a period ranging from about one-half minute to five minutes.

7. The method according to Claim 5, or 6 wherein said first application of an aqueous solution of an alkali silicate is made in a solution having a silica to alkali metal oxide ratio of at least 1:1.

8. The method according to any of the preceding claims in which the second application of an aqueous solution of alkali silicate is made with a solution having a silica to alkali metal oxide ratio of from 1:1 to about 4:1.

9. The method according to Claim 1 in which said first bath is water at a temperature of at least 150° F.

10. The method according to Claim 9 in which the second bath comprises an aqueous solution of 0.1% to 30% of an alkali metal silicate in which the ratio of silica to alkali metal oxide is in the range of about 1:1 to about 4:1.

11. The method according to Claim 1 in which the first bath comprises an aqueous solution of a material of the group consisting of alkali dichromates, alkali chromates and chromic acid.

12. The method of treating aluminum having a porous oxide coating thereon to produce increased resistance to corrosion substantially as hereinbefore described with reference to any of Examples I to XI.

13. Aluminum having a porous oxide coating thereon when treated in accordance with the method set forth in any of Claims 1—12.

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